The Secondary Structure in Crystals.

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IT has been increasingly recognised in recent years that the simple lattice theory of crystals is not enough to account for the various physical properties of the crystalline state of matter. The existence of a sharp melting point, the accurate lining up of crystalline planes over macroscopic distances, the enormous influence in the physical (particularly magnetic) properties due to the absorption of foreign atoms and the volume effects of crystal grains of macroscopic sizes—these have been advanced by Zwicky as properties which need a revision of the simple lattice theory. To these we may add the regularity of a disperse system of foreign atoms in a crystal as revealed by X-ray spectra, the difficulties of a satisfactory explanation of ferromagnetism on the atomic basis, the existence of anomalous diamagnetism in some crystals as those of bismuth and graphite and the little-understood properties of elasticity (particularly fatigue, after-effect and elastic limit).

The simple lattice theory involves an accurate spacing up of like or unlike atoms in different directions, the interaction between neighbouring atoms being electrostatic or electron linked. It should be mentioned here that while a secondary (as distinguished from the primary or simple lattice) structure seems to be necessary for a proper understanding of several well-known properties, a simple physical picture of such a structure has not yet been conclusively developed.

Zwicky postulates a microcrystal block in a crystal as a region surrounded by a surface physically different from a similar surface taken within the block. This would suggest that the interatomic distance is smaller nearer the surface than inside the block. Zwicky estimates, for example, that the surface of such a block in rocksalt crystal contains 10% more atoms per unit area than in the inter-lattice planes. If such a microscopic structure is identical with the spontaneously magnetised blocks of Heisenberg in his theory of ferromagnetism, it would follow that the surface of these blocks would not merely correspond to the regions of largest crowding of the atoms but also those across which the electrons are not ferromagnetically coupled with each other.

Zwicky's calculations, based on the small differences observed between the X-ray wavelengths obtained by crystal and grating methods, lead him to a value of nearly 100 A.U. for the linear dimension of the rocksalt block. This would suggest that a block contains nearly 43,000 atoms. Bitter's results based on ferromagnetic data give a value of nearly 10^5 atoms in a microcrystal. These results also indicate that the dimension of the block is of the order of 100 A.U.

It may be pointed out that the secondary structure should give rise to a secondary spectrum in the Bragg reflections; however, since for every 30 planes in the above case we have a secondary surface, the grating obtained is very inefficient. However, Johnson reflected H atoms from a crystal of LiFl and obtained a secondary spectrum which indicated the lattice constant to have a value somewhere between 50 and 100 A.U. It is interesting to mention here the investigations of Jaegar and Zanstra on the crystal structure of rubidium. They found the co-existence of two phases, one phase being present in the other in the form of small blocks containing 36,000 atoms; this leads to a value of nearly 100 A.U. for the secondary lattice constant. It is significant that four different methods have all suggested the same order of value for the dimension of the microcrystal.

We shall now consider some special directions in which the experimental observations fully conform to Zwicky's theory and in fact would not have any other rational explanation except on this basis. First we shall take up the question of the solution of one metal in another. G. L. Clark gives an excellent account of our present knowledge of this subject in his book on *Applied X-rays*. Three cases can be broadly distinguished. In the first case, the atoms of the foreign body B replace or crowd into the lattice atoms of the given metal A. Such a crowding produces a shift in the lines of the X-ray spectra indicating smaller lattice constants. The second case arises when there are both types of microcrystals in the alloy; the characteristic spacings of both the lattices being present in the X-ray spectra. The third case arises when chemical combinations take place involving predominantly combinations of covalent atoms; these give rise to new spacings of the lattice as revealed by X-ray spectra. It is difficult to understand these distinctions on any satisfactory basis on the simple lattice theory but once we grant the theory of secondary structure, the whole picture becomes intelligible. In the type 2, both sets of microcrystals are co-existent in the alloy in large groups while in the first case the foreign atoms are able to permeate through the microcrystal surfaces into the blocks. The relative quantities of the two constituents settle the nature of the structure of the alloy. At present there is no satisfactory basis for the energy calculations in such cases but there is little doubt that the nature of the permeation of the foreign atoms in the given crystal is fixed by energy considerations. A development along these lines is necessary if the theory of secondary structure is to be placed on a satisfactory quantitative basis.

It is interesting to note that the strongly ferromagnetic iron and the strongly diamagnetic bismuth do not dissolve in each other. This result is significant from the point of view of secondary structure since it seems possible that the consolidating tendencies of the microcrystals of these metals are too strong for the disruption of the individual microcrystals.

Another important observation that needs special notice is that when small quantities of a foreign metal are alloyed with the given metal, the lattice constant does not alter while there is a large alteration in the magnetic susceptibility. On the simple lattice theory it is doubtful whether a reasonable explanation can be given for this observation. On the theory of the secondary structure in crystals, this would mean that the foreign atoms place themselves on the microcrystal borders and while influencing greatly the magnetic properties so largely dependent on the large electron orbits on the microcrystalline surfaces, do not affect the lattice constant predominantly settled by the interior atoms.

That the foreign atoms stay in the microcrystal borders is beautifully verified by the lower melting point in general of the alloys; since the disruptive tendency between the microcrystals amplified by the presence of the foreign atoms, is mainly responsible for melting. These microcrystals, with their borders very fuzzy and their internal structure rendered less stable, account for the persistence of a crude crystal structure in liquids just after melting. As the liquids are heated this structure is broken rapidly.

The writer has recently investigated the magnetic properties of colloidal powders of strongly diamagnetic and ferromagnetic metals. As a result of these observations and the recent investigations of Goetz, there is abundant evidence to show that when the colloidal powders approach small diameters of the order of 1μ, large changes take place in their magnetic properties. The X-ray spectra of such colloidal powders appear to pass over from those corresponding to crystal powders to those of liquids, at smaller diameters. In certain experiments conducted by the writer some three years ago on the conductivity of compressed colloidal powders of Ceylon graphite the specific conductivity of particles having diameters less than about 1 to 2μ, was larger than of those having larger diameters. The investigations were not pursued at the time since the explanation of such an observation remained obscure. It now appears, however, that such an effect may be genuine and may be accounted for by proportionately greater surface conductivity. Thus the particles having diameters greater than about $1{\cdot}5\mu$ differ in properties from those having smaller diameters. The writer has shown recently that this may be due to the destruction of a large number of microcrystals on the surface of the macrocrystals.

It is significant that Goetz, to whom we owe a large amount of useful and pioneer work on magnetism and crystal structure, has found that the crystal planes line up regularly over macroscopic distances. A similar secondary structure has been observed by Bitter in magnetised crystals of nickel and iron.

In the theory of ferromagnetism, the secondary structure in crystals plays a predominant part. It is well known that Heisenberg's theory of ferromagnetism postulates the existence of a large number of microcrystals in a crystal. The resultant spins in these microcrystals have random orientations and compensate each other in the absence of an external field. The large amount of work accomplished by various investigators on thin films and the recent work on nickel colloids by Montgomery and the writer point to the correctness of the assumption of microcrystals in ordinary crystals.

Based on these, Bitter has given a theory of ferromagnetism by which he has accounted for the properties of hysteresis and the Curie points in ferromagnetic bodies.

There is one other direction in which theoretical work should be of great significance in the proper understanding of these problems. Tartakowsky and Kudrjawzewa found that the total secondary electron emission from heated nickel decreases suddenly at the temperature corresponding to the Curie point of this metal. Hayakawa has used this method to study transformations from one state to another in metals. The structure electrons of Richardson should be responsible not only for secondary emission but also for conserving the total spin in a microcrystal so necessary for Heisenberg's theory. If these conclusions are true, it would follow that the regions of the secondary structure around the microcrystals are filled with electron energy levels having a maximum energy of at least 400 volts, and that in this manner the structure electrons are responsible for the Zwicky blocks.

It should be mentioned here that the theory of secondary structure is not without its limitations. Smekal claims that the results obtained with shearing stresses in crystals, particularly in rocksalt, definitely indicate the existence of only an ideal lattice. While therefore the problem of the Zwicky structure in crystals like rocksalt may be an open question, there seems to be, from what we have explained in this article, very little doubt regarding the existence of such a structure in metallic crystals.

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The Incidence of Silicosis in Kolar Gold Fields, Mysore.

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IT was the impression till recently that there were no cases of silicosis among the miners of Kolar Gold Fields. In the report of "The Miners' Phthisis Conference, South Africa" it is mentioned that no case of silicosis has been reported from K.G.F. While silicosis was so common in other gold mining areas, such as South Africa, that no case had been reported from K.G.F. was really surprising. It was suggested that an investigation may be started to find out the existence or not of silicosis in K.G.F. A committee was formed in 1931 to collect material and to study the peculiar conditions existing in this mining area.

Clinical histories of about one hundred labourers working underground were collected. Seventy-five chest radiograms were taken. As a control, radiograms of twenty people unconnected with underground work were also taken. Three lung specimens removed, Post Mortem of labourers who died of respiratory diseases were made available for study. Sections were prepared and examined by Pathologists.

After a careful study of this material it was concluded that cases of silicosis do exist in K.G.F. Only, it takes ten to fifteen years of underground work to develop signs of silicosis. It is due to the fact that the quartz reef in K.G.F. contains only 8 to 17% of free silica as compared to the high percentage, namely, 80 to 90 in the South African rock. The collected material was sent to "The Bureau of Medical Research, South Africa," for expert opinion.

Dr. L. G. Irvine and Dr. S. W. Simson were kind enough to give their opinion after studying the material sent to them. Dr. Irvine reports "The Pathological and Radiographic evidence appears to create a *prima facie* case that instances of Silicosis do occur amongst underground workers in the Kolar Gold Mines." He also adds that the material forwarded was inspected by Dr. A. Mavogordato who concurs in the